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Synthesis and Properties of Copper(II) Tetra(2-alkyl-4,5-benzimidazolo)- and Tetra(2,2'-Dimethyl-4,5-benzodiazepino)porphyrazines

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Abstract—4,5-Diaminophthalonitrile was reacted with carboxylic acids and acetylacetone to synthesize 2-alkyl-5,6-dicyanobenzimidazoles and 2,2'-dimethyl-5,6-dicyanobenzodiazepine, respectively. The products were converted into copper(II) porphyrazines. An effect of the heterocyclic residue on the physicochemical and spectral properties of the porphyrazines was revealed.

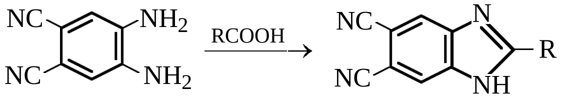
One of interesting ways to modifying phthalocyanine molecules is their peripheral substitution by heterocyclic residues, such as imidazole and diazepine.

The practical interest in these compounds is associated with the fact that benzimidazole substituents impart to macroheterocycles fluorophoric properties [1]. Moreover, the combination in the imidazole structure of both pyrrole and pyridine nitrogen atoms makes possible diverse chemical modification of these compounds.

The synthesis and properties of tetraazaporphynes with annelated imidazole and diazepine residues have been reported [2, 3]. The information on phthalocyanine analogs of these systems is limited by our communication concerning the synthesis and properties of 5,6-dicyanobenzimidazole and its pophyrazine derivatives [4]. Proceeding with this work and aiming at assessing the effect of the annelated heterocyclic residue on the physicochemical properties of porphyrazines, we synthesized copper(II) tetra(2-alkyl-4,5-benzimidazolo)- and tetra(2,2'-dimethyl-4,5-benzodiazepino)porphyrazines.

The starting material in the synthesis of 2-alkyl-5,6-dicyanobenzimidazoles **II**–**IV** and 2,2'-dimethyl-5,6-dicyanobenzodiazepine (**V**) was 4,5-diaminophthalonitrile (**I**) synthesized by reduction of 5-amino-4-nitrophthalonitrile with tin dichloride in concentrated hydrochloric acid [4].

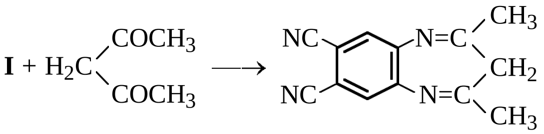
4,5-Diaminophthalonitrile (**I**) was reacted with an excess of a carboxylic acid (acetic, butyric, capronic) under reflux to obtain 2-methyl-, 2-propyl, and 2-pentyl-5,6-dicyanobenzimidazoles (**II**–**IV**).



I **II**–**IV**

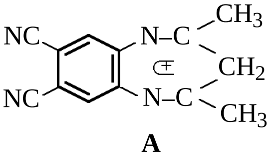
R = CH_3 (**II**), C_3H_7 (**III**), C_5H_{11} (**IV**).

2,2'-Dimethyl-5,6-dicyanobenzazepine was synthesized by reaction of diamine **I** with a slight excess with acetylacetone.



V

The powder-like colorless (**II**, **III**) or light yellow (**IV**) benzimidazoles are soluble in hot water, DMF, acetone, dilute acids and alkalis, while the powder-like colorless benzodiazepine **V**, in DMF, acetone, dilute HCl and, poorly, in alcohols. The HCl solution is violet, on account of the formation of a stable salt **A** [5].



A

The structure and composition of compounds **II**–**V** were proved by elemental analysis and IR spectroscopy.

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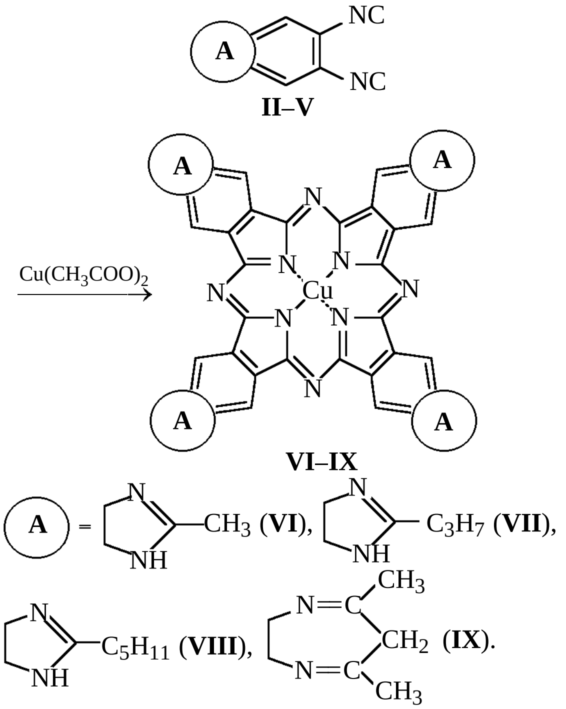
The IR spectra of compounds **II**–**V** have common absorption bands. Thus, in the 2240–2232 cm^{-1} range, there are bands characteristic of cyano groups, while at 1664 cm^{-1}, an absorption band characteristic of the imidazole and diazepine C=N band [6]. Compounds **II**–**IV** give C–H and C–C absorption bands at 2936–2928 and 720–704 cm^{-1}, respectively, and the intensity of these bands increases with increasing alkyl chain length [6].

The formation of the imidazole ring is also evidenced by the fact that the products acquire solubility in aqueous mineral acids and alkalis, on account of the presence in their molecules of a pyrrole and a pyridine nitrogen atoms.

Compounds **II**–**V** were used for preparing copper porphyrazines **VI**–**IX**. The synthesis of complexes **VI**–**IX** was accomplished by fusing nitriles **II**–**V** with copper(II) acetates at 250°C for 1 h.



II–**V**

VI–**IX**

The powder-like bluish-green complexes **VI**–**IX** are insoluble in water, readily soluble in concentrated sulfuric acid, and much worse soluble in DMF and dilute hydrochloric acid.

Four methyl substituents in the tetrabenzimidazolopophyrazine molecule do not render it more soluble in organic solvents, whereas four propyl or four pentyl groups make it slightly soluble in chloroform or acetone, respectively.

Complexes **VI**–**IX** were characterized by elemental analysis and IR and electronic spectroscopy.

The IR spectra of compounds **VI**–**IX** proved to be difficult to assign, since the absorption bands are broadened and overlapping, on account of solid-state association effects.

The heterocyclic substituents strongly affect the electronic absorption spectra. Compounds **VII** and **VIII** in DMF give two bands at 642–650 and 694–711 nm, whose intensity depends on the porphyrazine concentration. Thus, dilution produces growth of the long-wave band and diminishing of the short-wave band. Such behavior points to the association of the porphyrazines in the solution via hydrogen bonding involving the imidazole fragments. Apparently, the absorption band at 642–650 nm relates to associated forms, while that at 694–711 nm, to monomeric.

We could not compare the electronic absorption spectra in DMF for all the compounds studied, since copper(II) tetrabenzimidazolo- and tetrabenzodiazepinoporphyrazines, as well as copper(II) phthalocyanine are sparingly soluble in this solvent. Therefore, we compared the electronic absorption spectra in concentrated sulfuric acid.

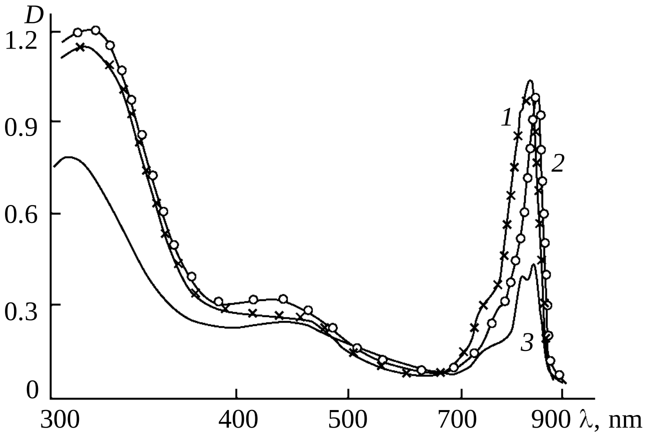
In going from organic solvents to concentrated sulfuric acid, the *Q* bands of compounds **VII** and **VIII** shift bathochromically by 90 nm, which is associated by the protonation of the molecule both by the *meso*-nitrogen atoms of the porphyrazine ring, as well as by the nitrogen atoms of the heterocyclic fragments [7]. The occurrence of the two protonation processes makes the absorption bands difficult to assign.

It should be noted that the bathochromic shift of the *Q* band also increases with increasing chain length in the alkyl substituent, since the enhancing basicity of the imidazole pyridine atoms produces a more profound protonation (see figure). The electronic absorption spectrum of diazepine derivative **IX** shows two more long-wave absorption bands compared with the spectrum of copper(II) phthalocyanine (see figure).

EXPERIMENTAL

The electronic absorption spectra were measured on a Hitachi UV-2000 spectrophotometer, and the IR spectra, on a Specord M-80 spectrophotometer.

2-Alkyl-5,6-dicyanobenzimidazoles II–**IV.** A mixture of 87.4 mmol of carboxylic acid and 6.3 mmol of compound **I** was heated under reflux for 2 h, cooled to room temperature, and poured into 50 ml of water with ice. The precipitate that formed was filtered off, washed with water, recrystallized from water, and dried at 120°C.



Electronic absorption spectra of copper(II) porphyrazines in concentrated sulfuric acid (*c* 5×10^{-6} M). (*1*) Copper tetra(2-propyl-4,5-benzimidazolo)porphyrazine (**VII**), (*2*) copper tetra(2-pentyl-4,5-benzimidazolo)porphyrazine, and (*3*) copper tetra(2,2'-dimethyl-4,5-benzodiazepino)porphyrazine (**IX**).

2-Methyl-5,6-dicyanobenzimidazole (II), yield 61%, mp 243–245°C. IR spectrum, ν, cm^{-1}: 3416 (NH), 2936 (CH), 2232 (CN), 1664 (C=N), 1600 (C=C), 720 (C–C). Found, %: C 66.0; H 3.5; N 30.6. $C_{10}H_6N_4$. Calculated, %: C 65.9; H 3.3; N 30.8. **2-Propyl-5,6-dicyanobenzimidazole (III),** yield 38%, mp 239–241°C. IR spectrum, ν, cm^{-1}: 3416 (NH), 2930 (CH), 2232 (CN), 1664 (C=N), 1600 (C=C), 716 (C–C). Found, %: C 68.9; H 4.7; N 26.4. $C_{12}H_{10}N_4$. Calculated, %: C 68.6; H 4.8; N 26.7. **2-Pentyl-5,6-dicyanobenzimidazole (IV),** yield 40%, mp 235–237°C. IR spectrum, ν, cm^{-1}: 3416 (NH), 2936 (CH), 2232 (CN), 1664 (C=N), 1600 (C=C), 704 (C–C). Found, %: C 71.1; H 5.9; N 23.0. $C_{14}H_{14}N_4$. Calculated, %: C 70.6; H 5.9; N 23.5.

2,2'-Dimethyl-5,6-dicyanobenodiazepine (V). A mixture of 3 mmol of acetylacetone and 3 mmol of compound **I** in 20 ml of ethanol and 0.06 ml of glacial acetic acid was heated under reflux for 2 h, cooled to room temperature, and poured into 50 ml of water with ice. The precipitate that formed was filtered off, washed with water, recrystallized from water, and dried at 120°C. Yield 35%, mp 218–222°C. IR spectrum, ν, cm^{-1}: 3416 (NH), 2936 (CH), 2240 (CN), 1664 (C=N), 1600 (C=C), 704 (C–C). Found, %: C 70.5; H 4.8; N 25.5. $C_{13}H_{10}N_4$. Calculated, %: C 70.3; H 4.5; N 25.2.

Copper tetra(2-alkyl-4,5-benzimidazolo)porphyrazines VI–IX. A mixture of 0.6 mmol of compound **II**–**IV** and 0.17 mmol of copper(II) acetate was heated at 250°C for 1 h. The melt was thoroughly ground and dissolved in a minimum (10–50 ml) of concentrated sulfuric acid. The solution was poured into 50 ml of water. The precipitate that formed was filtered off, washed with water to neutral, and purified by treatment with hot acetonitrile.

Copper tetra(2-methyl-4,5-benzimidazolo)porphyrazine (VI), yield 45%. Electronic absorption spectrum, λ_{max}, nm (H_2SO_4): 310, 761. Found, %: C 60.8; H 3.1; N 28.0. $C_{40}H_{24}CuN_{16}$. Calculated, %: C 60.6; H 3.0; N 28.3. **Copper tetra(2-propyl-4,5-benzimidazolo)porphyrazine (VII),** yield 38%. Electronic absorption spectrum, λ_{max}, nm: in DMF: 643, 694; in H_2SO_4: 310, 426, 786. Found, %: C 64.0; H 4.8; N 24.1. $C_{48}H_{40}CuN_{16}$. Calculated, %: C 63.7; H 4.4; N 24.5. **Copper tetra(2-pentyl-4,5-benzimidazolo)porphyrazine (VIII),** yield 67%. Electronic absorption spectrum, λ_{max}, nm: in DMF: 650, 711; in H_2SO_4: 310, 426, 802. Found, %: C 66.6; H 5.8; N 21.8. $C_{56}H_{56}CuN_{16}$. Calculated, %: C 66.1; H 5.5; N 22.0.

Compounds **VI**–**IX** are poorly soluble in DMF, acetone, chloroform, and aqueous mineral acids and alkalis, and readily soluble in concentrated sulfuric acid.

Tetra(2,2'-dimethyl-4,5-benzodiazepino)porphyrazine (IX) was prepared in a similar way from 0.5 mmol of compound **V** and 0.15 mmol of copper(II) acetate, yield 27%. Electronic absorption spectrum, λ_{max}, nm (H_2SO_4): 310, 772, 798. Found, %: C 65.7; H 4.5; N 23.2. $C_{52}H_{40}CuN_{16}$. Calculated, %: C 65.5; H 4.2; N 23.5.

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